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71 Applicant: **E.C.C. AMERICA INC.**  
**5775 Peachtree-Dunwoody Road N.E. Suite 200 G**  
**Atlanta Georgia 30342 (US)**

72 Inventor: **Prescott, Paul L.**  
**150 Rockbridge Road**  
**Lilburn, Georgia 30247 (US)**

**Rice, Camilla Arlyn**  
**634 W. Church Street Sandersville**  
**Georgia 31082 (US)**

74 Representative: **Bull, Michael Alan et al**  
**Haseltine Lake & Co. Hazlitt House 28 Southampton**  
**Buildings Chancery Lane**  
**London WC2A 1AT (GB)**

54 Surface modified pigments and methods for producing same and elastomers containing same.

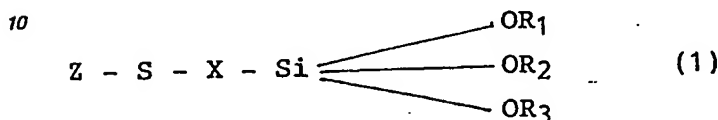
57 The surface of a hydrous clay, such as kaolin, is modified by treatment with an alkyl dimethoxy mercaptopropylsilane and the modified clay is used as a filler in elastomers to give improved reinforcement.

## Description

SURFACE MODIFIED PIGMENTS, METHODS FOR PRODUCING SUCH PIGMENTS AND ELASTOMERS CONTAINING SUCH PIGMENTS

This invention relates to inorganic pigments and, more particularly, is concerned with modifications of inorganic pigments, e.g., clays. In particular, the present invention is concerned with the modification of finely divided particulate clays such as kaolin clays by treatment with mercaptopropylsilanes to improve their usefulness as reinforcing fillers in rubber.

It is known from US-A-3567680 that mercaptopropyl silanes having the formula:



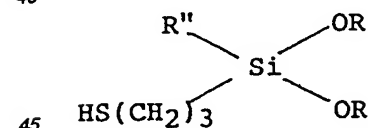
In which Z is chosen from hydrogen, cation, alkyl, aryl, alkylaryl, arylalkyl and derivatives thereof; X is chosen from alkyl, alkylaryl and arylalkyl; and R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>, are chosen from hydrogen, cation and alkyl, are suitable for modifying kaolin clays to enable them to be used as reinforcing fillers for elastomers. In fact, the thus modified clays have been the candidates of choice for such fillers in commerce. It may be noted that, in US-A-3567680, only the trialkoxymercaptopropyl silanes are considered.

In US-A-3364059, a method for treating glass fibres to improve their bonding relationship to rubbers is disclosed. The method comprises treating them with a silane which has from 1 to 3 highly hydrolyzable groups and an organic group attached to the silicon atom containing a thio group, as represented by the formula R<sub>n</sub>SiX<sub>(4-n)</sub> wherein X is a highly hydrolyzable group such as halogen (e.g. chlorine, bromine, iodine), methoxy, ethoxy, propoxy or another similar short-chained alkoxy group.

In US-A-4143027, mercaptosilane powder mixtures are described having a superior shelf life and which are added during compounding of rubbers to provide a desirable amount of the silane therein. The object is to absorb a silane on a powder and achieve good storage stability. Example 1 of US-A-4143027 shows a rubber composition comprising a hydrous clay-filled polyisoprene, various additives and the silane powder mixture, the silane compounds described being the trimethoxy, -ethoxy and -n-propoxy mercaptopropyl silanes of which the latter two are stated to exhibit far greater stability in storage than the methoxy compounds.

It has now been unexpectedly found that a different structure of mercaptopropyl silanes is more desirable as a modifier of clays, producing more effective reinforcing fillers for materials such as elastomers and plastics. The treated materials show unexpected improvements in tear resistance and also better stock-to-stock adhesion.

According to a first aspect of the present invention, there is provided a finely divided particulate reinforcing material suitable as a filler for an elastomer, comprising a hydrous clay, the surface of which has been modified by treatment with a mercaptosilane, characterised in that the mercaptosilane is of the following general formula :



wherein R is an alkyl radical and R'' is an alkyl radical or an aryl radical.

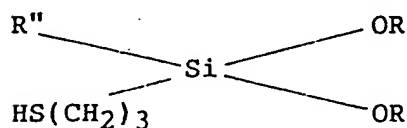
Preferably, R'' is a lower alkyl radical such as methyl or ethyl or an aryl radical such as phenyl. Preferably, R is a lower alkyl having from one to four carbon atoms.

Silanes of the structure used in the present invention are commercially available as Dynasylan 3403, as advertised in a brochure of Dynamit Nobel, Kay-Fries Chemical Division entitled "Dynasylan Organo Functional Silanes/Coupling Agents".

The clay employed as starting material may be any hydrous clay, for example one that has not been calcined, i.e. dehydroxylated, since the hydroxyl groups are needed in the treatment with the silane. Most preferably, the hydrous clay is a kaolin clay. With regard to terminology, it may be noted that although the term "hydrous" is commonly used, strictly speaking there is no molecular water actually present in the kaolinite structure as it is now well known that kaolinite is an aluminium hydroxide silicate of approximate composition Al<sub>2</sub>(OH)<sub>4</sub>Si<sub>2</sub>O<sub>5</sub>. Commercially available clays useful for the present purpose include kaolins such as Alphaplate<sup>®</sup>, which is a delaminated kaolin, having 80% by weight of its particles below 2 micrometers; Alphagloss<sup>®</sup> (94-96% less than 2 micrometers); and Betagloss<sup>®</sup> (94-96% less than 2 micrometers). These and other suitable kaolins are available from the Anglo-American Clays subsidiary of E.C.C. America, Inc. of Atlanta, Georgia.

It is believed that the improvement in the modified clays of the present invention, as reinforcing fillers for rubber, may arise from a change in their stereochemistry and/or in their hydrophobicity.

According to a second aspect of the present invention, there is provided a method for reinforcing elastomers comprising the steps of: (i) modifying the surface of a hydrous clay by treatment of the clay with from 0.2 to 0.7% by weight, based on the weight of the dry clay, of a mercaptosilane having the general formula :

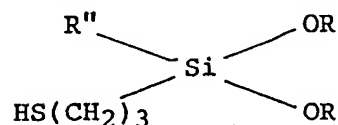


in which R is an alkyl radical and R'' is an alkyl radical or an aryl radical; and (ii) combining the thus surface modified clay with an elastomeric material.

Preferably, from 0.25% to 0.45% of the mercaptosilane, based on the weight of the dry clay, is added to the slurry.

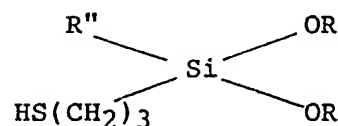
As previously mentioned, the hydrous clay is preferably a kaolin.

According to a third aspect of the present invention, there is provided a reinforced elastomer comprising an elastomeric material and, as a filler, a hydrous clay the surface of which has been modified by treatment with a mercaptosilane having the general formula :



in which R is an alkyl, and R'' is an alkyl radical or an aryl radical.

According to a fourth aspect of the present invention there is provided a process for preparing a finely divided particulate mercaptosilane surface treated clay suitable for use as a filler for an elastomer, which process comprises: preparing a dispersed aqueous clay slurry; adding to said slurry, in an amount of from 0.2 to 0.7% by weight, based on the weight of the dry clay, of a mercaptosilane of the following formula :



wherein R is an alkyl radical and R'' is an alkyl radical or an aryl radical; and spray drying said slurry to produce said mercaptosilane surface modified clay.

Typically, a kaolin clay is mined and the crude is subjected to conventional beneficiation procedures, which may include such steps as magnetic separation and bleaching. The kaolin is isolated, for example by flocculation and filtering. The filter cake is then redispersed in water to form, for example, a 50% to 60% solids slurry and mixed with a mercaptosilane of the formula used in the present invention. The reaction is almost instantaneous. The slurry may then be spray dried to give the modified clay product.

A typical formulation with rubber comprises 75 parts by weight filler to 100 parts rubber, together with modifiers, aids, and the like as shown in Formulation 1. The trade names used throughout are identified in Table 9

Formulation 1

	<u>Ingredient</u>	<u>Parts by Weight</u>
	Natsyn 2200	100.0
5	ZnO	5.0
	Stearic acid	2.0
	Agerite white	1.0
10	OBTS	1.25
	TMTD	0.2
	Sulphur	2.75
15	Mercaptosilane treated clay	<u>75.0</u>
	Total	187.2

20 When rubber formulations such as these are subjected to conventional curing, the resultant products are found to have superior characteristics, in terms of, for example, improved tear resistance and improved stock-to-stock adhesion, in comparison to products including prior art silane treated clay fillers.

25 Extensive studies showed surprisingly superior properties for the products of the present invention. In these studies, the silane employed was an alkyl dimethoxy mercaptopropylsilane, e.g., methyl dimethoxy mercaptopropylsilane, and it was used to treat five different hydrous kaolin clays. Typical physical properties of silane treated clays in accordance with the present invention are given in Table 1. These products were prepared using amounts of the mercaptosilane in the range of from 0.25 to 0.45% by weight, based on the weight of the dry clay.

Table 1

Mercaptosilane Treated Hydrous ClaysTYPICAL PROPERTIES

PRODUCT DESIGNATION:	P1	P2	P3	P4	P5
G.E. Brightness %	87-90	85-88	90-92	85-88	90-92
Specific Gravity	2.63	2.63	2.63	2.63	2.63
Particle Size, in % less than 2 microns	80	92	95	92	95
Particle Size, Avg. microns	.40	.25	.20	.25	.20
pH (3)	7.0	7.0	7.0	7.0	7.0
Screen Residue, % max. (325 mesh, i.e. 0.045mm nominal aperture) (2)	.01	.01	.01	.01	.01
Moisture, % max. (1 Hr. @ 105°C) as packaged (1)	1.0	1.0	1.0	1.0	1.0
Bulk Density kg/m <sup>3</sup> (lbs/ft <sup>3</sup> )	800 (50)	800 (50)	800 (50)	800 (50)	800 (50)

1. ASTM D280

2. ASTM D1514

3. pH (+/- 0.5)

100 g clay; 250 ml water

The treated clays impart these properties to rubber compositions:

1. High modulus
2. Low Hysteresis
3. Improved Tear Resistance
4. Improved Stock-to-Stock Adhesion
5. Good Heat Aging Properties
6. Low Viscosity Levels (relative to loading)
7. Improved permeability resistance to Air, Gas, and Moisture

These and other advantages of the present invention will be illustrated by the following non-limiting Examples.

Example 1

This example is illustrative of the use of the present invention in passenger car tyre white sidewall (WSW) portions of a tyre body. The WSW-I formulation defined below was tested against similar formulations containing prior art products A and B which were treated in a similar process using trimethoxy mercaptopropylsilane instead of the dialkoxo mercaptosilanes used in the present invention. The physical properties of these systems are provided in Table 2.

WSW-I Formulation

SMR-5	30.00
EPDM	10.00
Chlorobutyl Rubber	60.00
Treated Clay	40.00
TiO <sub>2</sub>	25.00
ZnO	5.00
Wax	5.00
Stearic Acid	1.00
U-M Blue	0.40
Vultac 5	1.00
MBTS	0.75
Sulphur	0.50
TOTAL	148.65

Table 2

Mercaptosilane Treated Clay P4 vs. Prior Art  
Product A

Mercaptosilane Treated Clay P5 vs. Prior Art  
Product B

<u>Cured 20 min. @ 160°C</u>	<u>A</u>	<u>P4</u>	<u>B</u>	<u>P5</u>
300% Modulus kg/sq.cm.	45	39	39	46
Tensile kg/sq.cm.	116	140	130	138
Elongation %	550	600	650	600
Hardness Shore A	56	56	55	57
Trouser Tear kg/cm.	13.9	15.7	13.6	16.6
Stock-to-Stock				
Adhesion kg/cm.	3.2	4.1	3.2	5.4

In this high chlorobutyl rubber tri-blend composition, both the P4 and P5 treated clays are compared with their respective prior art counterparts.

Both treated clays provide superior tear resistance and stock-to-stock adhesion with the P5 treated rubber being the most effective. All testing procedures used in this and the following examples are ASTM as identified in Table 10.

Example 2

In this second Example using the WSW-II formulation, which is higher than WSW-I in natural rubber content, the P5 product is compared with the prior art B product.

WSW-II Formulation

	<u>C</u>	<u>D</u>	
Vistalon 4608	20.00	20.00	
SMR-5	60.00	60.00	5
HT 1066	20.00	20.00	
TiO <sub>2</sub>	30.00	30.00	
Silane Treated Clay P5	40.00	-----	
Prior Art B Product	-----	40.00	10
Platey Talc	20.00	20.00	
MgO	.50	.50	
U-M Blue	.20	.20	
Stearic Acid	1.00	1.00	15
ZnO	5.00	5.00	
Insol. Sulphur	.67	.67	
MBTS	.75	.75	
Vultac 5	1.25	1.25	20
TOTALS	199.37	199.37	

Table 4WSW-II Formulation Data

<u>Cured 45 min. @ 149°C</u>	<u>C</u>	<u>D</u>	
Modulus 100% kg/sq.cm.	25.3	20.4	30
200% kg/sq.cm.	44.9	37.9	
300% kg/sq.cm.	63.3	55.5	
Tensile kg/sq.cm.	135.0	128.0	
Elongation %	530	550	35
Trouser Tear kg/cm. RT	6.8	2.6	
kg/cm. 100°C	4.8	3.1	

Formulation C (including the treated clay P5) exhibits higher modulus than Composition D (Including prior art clay B), which translates to improved buffing. Hot tear resistance is also superior by a significant margin.

The treated clay P5 also has a high G.E. Brightness of 90-92 and can be considered as a partial replacement for TiO<sub>2</sub> in WSW and in other colour applications. The cost advantage of such a substitution is also attractive.

EXAMPLE 3

Example 3 demonstrates the advantages of using one of the products of this invention in a tyre innerliner. The formulation is given below :

INNERLINER FILLER RATIOS

	<u>F</u>	<u>G</u>	<u>H</u>	
HT1068	100	100	100	
N660	70	45	-	55
N650	-	-	45	
Hard Clay	24	-	-	
Silane Treated Clay P1	-	50	50	60

N660 and N650 are recognized trade carbon blacks used by the rubber industry in tyre applications.

The control, composition F, uses a conventional mix of N660 (carbon black) blended with an untreated hard clay. Compositions G and H blend the silane treated clay P1 with N660 and N650 carbon blacks respectively.

The physical properties of the three compositions (F, G, H respectively) are given in Table 4 below.

The air permeability of compositions G and H show a significant increase in permeability resistance approaching the optimum that can be imparted by incorporating a reinforcing mineral pigment. This advantage in increased resistance to air permeability is due not only to the crosslinking ability imparted by the mercaptosilane surface treated clay but also to the particle shape of the kaolin product: i.e. the P1 product is based on a delaminated kaolin.

**TABLE 4**  
**Innerliner Test Data**

Cured @ 145°C		Min.	F	G	H
Modulus	300% kg/sq.cm	45'	26.7	26.7	29.5
Tensile	kg/sq.cm	45'	84.4	91.4	86.5
Elongation	%	45'	700	780	700
Hardness	shore A	45'	55	55	55
Scorch	MS3 @ 121°C		30	30	30
Viscosity	ML4 @ 100°C		52	46	47
Monsanto Flex Fatigue		55'			
1,000 cycles RT (room temp.)			50.1	34.9	29.1
(70Hr @ 100°C) Aged			16.6	21.1	15.9
Air permeability					
(l/sq.m/24Hr/100 PA/0.075cm)			0.445	0.251	0.195

The stress-strain results are essentially, equivalent, with aged flex equal to, or better than, control for the compositions containing treated clay P1.

The improved permeability resistance obtained through carbon black reduction and replacement with treated delaminated clay permits:

1. An improved compound at reduced cost.
2. A reduction in overall chlorobutyl rubber content -- also a cost savings.
3. A possible gauge reduction (thickness) which would also reduce cost.

This improved permeability resistance can also offer advantages in systems such as fuel hose, Freon hose, and tank and pond liners.

#### Example 4

The advent of single ply roofing membrane has allowed the use of silane treated clays in both white and black compositions. Example 4 illustrates the use of these silane treated products of the invention in both compositions. The white EPDM roofing membrane formulation is given in Table 5 along with the physical property data.

The following white EPDM roofing study demonstrates the advantages of using treated clays P1 or P3 as (1) a reinforcing filler, (2) to extend TiO<sub>2</sub> (or partially to replace TiO<sub>2</sub> with these high GE brightness products), and (3) to provide a resistance to "crimping" before installation. Where optimum permeability resistance or a higher loading is desired, treated clay P1 would be preferred to treated clay P3.



0 265 223

Table 5White EPDM Roofing Formulation

	<u>I</u>	<u>J</u>	
Epsyn 5206	100.00	100.00	5
Irganox 1035	1.00	1.00	
ZnO	5.00	5.00	10
Silane Treated Clay P1	100.00	--	
Silane Treated Clay P3	--	100.00	
TiO <sub>2</sub>	25.00	25.00	15
Napthenic Oil	30.00	30.00	
Zn Stearate	1.00	1.00	
MBTS	0.75	0.75	
ZDBC.	0.75	0.75	
Sulfasan R	1.25	1.25	20
Sulfur	0.75	0.75	
TOTAL	265.50	265.50	25

White EPDM Roofing Data

<u>Cured 30 min. @ 160°C</u>		<u>I</u>	<u>J</u>	
Modulus 100% kg/sq.cm.	Orig.	28.2	21.1	
	Aged	59.1	47.8	35
	% Change	+52.4	+55.9	
Modulus 300% kg/sq.cm.	Orig.	44.4	43.0	
	Aged	78.7	88.6	40
	% Change	+42.8	+51.6	
Tensile kg/sq.cm.	Orig.	148.6	159.2	
	Aged	88.6	99.1	45
	% Change	-40.0	-37.6	
Elongation %	Orig.	740	750	
	Aged	440	420	50
	% Change	-40.5	-44.0	
Hardness Shore A	Orig.	65	63	
	Aged	80	78	55
	Change pts.	+ 15	+ 15	
Fluid Immersion	% Wt. Change	+ 4.4	+ 4.4	60

Aging Conditions: 28 days @ 100°C in air circulating oven; 24 hour recovery.

Fluid Immersion Conditions: 168 hours @ 100°C in distilled water with 1/2 hour recovery in 27°C distilled d 65

water.

The market for EPDM single ply roofing continues to expand. Chemically modified clays can be used as a reinforcing filler in black roofing compositions to help reduce cost.

The black EPDM roofing formulation is given in Table 6. Tables 7 and 8 show the physical properties of the unaged and aged test samples respectively.

These data show that treated clay P2 can be used partially to replace the carbon black content and meet all unaged and aged specifications.

TABLE 6

Black EPDM Roofing Formulation

Royalene 502	100.00
N660	85.00
Silane treated clay P2	100.00
Napthenic oil	95.00
ZnO	5.00
Stearic acid	1.00
MBT	1.50
TMTM	2.00
Sulphur	1.00
Diethylene glycol	<u>0.50</u>
TOTAL	391.00

Table 7

Black EPDM Roofing Data  
Unaged Physical Properties

<u>Cured 20 min. @ 160°C</u>			<u>Original</u>	<u>Specifications</u>
Modulus	100%	kg/sq.cm.	23.9	
	200%	kg/sq.cm.	52.7	
	300%	kg/sq.cm.	82.9	
Tensile		kg/sq.cm.	106.2	98.4 min.
Elongation		%	630	300 min.
Hardness		Shore A	62	60 to 70
Viscosity		ML4 @ 100°C	28.5	
Scorch		MS3 @ 121°C	11.0	
Trouser Tear		kg/cm.	18.9	5.4 min.

Table 8

Black EPDM Roofing Data  
Aged Physical Properties

<u>Cured 20 min. @ 160°C</u>		<u>Aged</u>	<u>% Change</u>	<u>Specifications</u>
Modulus	100% kg/sq.cm.	26.7	+ 10.5	
	200% kg/sq.cm.	59.7	+ 11.8	
	300% kg/sq.cm.	91.4	+ 9.2	
Tensile	kg/sq.cm.	101.2	- 4.6	- 28 max.
Elongation	%	560	- 11.1	- 25 max.
Hardness	Shore A	65	+ 3 pts.	
Fluid Immersion				
	% Vol. Change		+ 2.3	+ 8 max.
	% Wt. Change		+ 2.0	+ 8 max.
Low Temp. Brittle Point				
	Deg. °C	-56		- 52 min.
Ozone Resistance	Day 1	0		0 cracking
	Day 2	0		0 cracking
	Day 3	0		0 cracking
	Day 4	0		0 cracking
	Day 5	0		0 cracking
	Day 6	0		0 cracking

The aging conditions for the preceding test results were as follows :  
 Oven Aging: 7 days @ 70°C in an air circulating oven; 24 hour recovery.

Fluid Immersion: 166 hours @ 70°C in distilled water; 1/2 hour recovery in distilled water @ 27°C.  
 Low Temperature Brittle Point: 5 specimens each tested in 100% Methanol cooling medium.  
 Ozone Resistance: Exposure 7 days @ 40°C @ 100 pphm at 20% elongation; 24 hours prestretch @ 27°C;  
 rated every 24 hours.

Thus it can be seen that silane treated clays of the present invention have a higher safety factor with respect to tear and adhesion properties than can be achieved with prior art mineral filler products of another silane composition. They have the capability of partial replacement of carbon black. The novel products of this invention are the first low energy dependent mineral fillers which provide rubber properties similar to those of carbon black

Table 9

The following compounding ingredients are acknowledged  
as registered tradenames:

<u>Tradenname</u>	<u>Source</u>	<u>Compositional Type</u>
Natsyn 2200	Goodyear	Polyisoprene Rubber
Vultac 5	Pennwalt	Curing Agent
Vistalon 4608	Exxon Chemicals Americas	EPDM Polymer
HT1066, HL1068	Exxon Chemicals Americas	Halogenated Butyl Rubber
Mistron Vapor	Cypress Industrial Minerals Co	Talc
Epsyn 5206	CoPolymer Rubber	EPDM Polymer
Irganox 1035	Ciba-Geigy	Curing Agent
Sulfasan R	Monsanto	Sulfur Donor Curing Agent
Royalene 502	Uniroyal Chemical	EPDM
Agerite White	R.T. Vanderbilt	Antioxidant
Nordel 1070	DuPont	EPDM
Octamine	Uniroyal Chemical	Curing Agent
Hycar 1042	B.F. Goodrich	Nitrile Rubber
Krynac 870/60	Polysar	Nitrile PVC Rubber Blend
Wingstay 100	Goodyear Chemicals	Antioxidant
Methyl Zimate	R.T. Vanderbilt	Curing Agent
SMR-S		Standard Grade Natural Rubber
OBTS		Thiobenzothiazole
TMTD		Tetramethyl Thiuram Disulfide

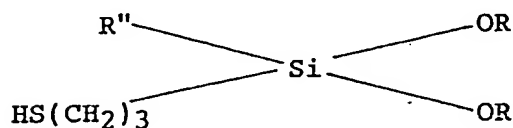
Table 10

ASTM D3182	Preparation of Materials
ASTM D412	Physical Properties
ASTM D2240	Hardness
ASTM D470	Modified Trouser Tear
ASTM D1646	Mooney Viscosity and Scorch
ASTM D623	Heat Generation and Plex Fatigue
ASTM D945	Compression Set
ASTM D573	Oven Aging

Firestone Procedure for Ply to Ply Adhesion

## Claims

1. A finely divided particulate reinforcing material suitable as a filler for an elastomer, comprising a hydrous clay, the surface of which has been modified by treatment with a mercaptosilane, characterised in that the mercaptosilane is of the following general formula :



wherein R is an alkyl radical and R'' is an alkyl radical or an aryl radical.

2. A reinforcing material as claimed in Claim 1, wherein R'' is a lower alkyl radical, preferably methyl or ethyl, or an aryl radical, preferably phenyl and R is a lower alkyl, preferably having from one to four carbon atoms.

3. A reinforcing material as claimed in Claim 1 or 2, wherein the hydrous clay is a kaolin that has not been dehydroxylated.

4. A reinforcing material as claimed in Claim 1, 2 or 3, wherein from 0.2% to 0.7% by weight of the mercaptosilane is used, based on the weight of the dry clay.

5. A reinforcing material as claimed in Claim 1, 2, 3 or 4, wherein the mercaptosilane is an alkyldimethoxy mercaptopropylsilane, preferably methyldimethoxymercaptopropylsilane.

6. A process for preparing a finely divided particulate mercaptosilane surface treated clay suitable for use as a filler for an elastomer, which process comprises: preparing a dispersed aqueous clay slurry; adding to said slurry, in an amount of from 0.2 to 0.7% by weight, based on the weight of the dry clay, of a mercaptosilane of the following formula :

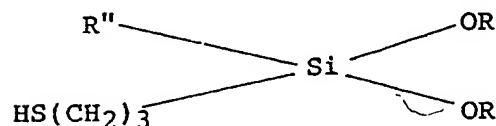


wherein R is an alkyl radical and R'' is an alkyl radical or an aryl radical; and spray drying said slurry to produce said mercaptosilane surface modified clay.

7. A process as claimed in Claim 6, wherein the clay is a kaolin that has not been calcined.

8. A process as claimed in Claim 6 or 7, wherein the mercaptosilane is an alkyldimethoxy mercaptopropylsilane, preferably a methyldimethoxy mercaptopropylsilane.

9. A method for reinforcing elastomers comprising the steps of: (i) modifying the surface of a hydrous clay by treatment of the clay with from 0.2 to 0.7% by weight, based on the weight of the dry clay, of a mercaptosilane having the general formula :



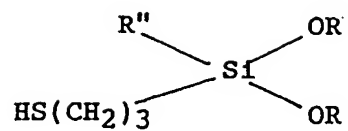
in which R is an alkyl radical and R'' is an alkyl radical or an aryl radical; and (ii) combining the thus surface modified clay with an elastomeric material.

10. A method as claimed in Claim 9, wherein the clay is a kaolin that has not been dehydroxylated.

11. A method as claimed in Claim 9 or 10, wherein the mercaptosilane is an alkyldimethoxy-mercaptopropylsilane, preferably methyldimethoxy mercaptopropylsilane.

12. A method as claimed in Claim 9, 10 or 11, wherein the elastomer forms part of a tyre.

13. A reinforced elastomer comprising an elastomeric material and, as a filler, a hydrous clay the surface of which has been modified by treatment with a mercaptosilane having the general formula :



in which R is an alkyl, and R'' is an alkyl radical or an aryl radical.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 87 30 9248

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 007 761 (J.M. HUBER CORP.) & US-A-3 567 680 (Cat. D) ----		C 09 C 1/42 C 08 K 9/06 C 08 L 21/00
A	EP-A-0 126 871 (DEGUSSA) ----		
A	CHEMICAL ABSTRACTS, vol. 94, no. 4, 26th January 1981, page 59, abstract no. 16901w, Columbus, Ohio, US; & SP-A-482 033 (TOLSA S.A.) 01-04-1980 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 09 C C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-12-1987	Examiner VAN BELLINGEN I.C.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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